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# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

# PCT

To:

GISLON, Gabriele  
MARIETTI E GISLON S.R.L.  
Via Larga, 16  
20122 Milano  
ITALIE



NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT.  
(PCT Rule 71.1)

Date of mailing  
(day/month/year)

14.09.2001

Applicant's or agent's file reference  
7526/675 (GG)

## IMPORTANT NOTIFICATION

International application No.  
PCT/EP00/05128

International filing date (day/month/year)  
05/06/2000

Priority date (day/month/year)  
04/06/1999

Applicant

JOHNSON CONTROLS AUTOMOTIVE S.R.L.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.


#### 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office - P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk - Pays Bas  
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl  
Fax: +31 70 340 - 3016

Authorized officer

Sinanovic, E

Tel. +31 70 340-2672



# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


Applicant's or agent's file reference 7526/675 (GG)		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/409)	
International application No. PCT/EP00/05128	International filing date (day/month/year) 05/06/2000	Priority date (day/month/year) 04/06/1999	
International Patent Classification (IPC) or national classification and IPC C08L23/10			
Applicant JOHNSON CONTROLS AUTOMOTIVE S.R.L.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
  - ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☒ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  15/12/2000	Date of completion of this report  14.09.2001
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer  Schmidt, H  Telephone No. +31 70 340 2461



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/05128

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-14 as originally filed

**Claims, No.:**

1-14 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

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(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

## III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- ☐ the entire international application.
- ☒ claims Nos. 2,4,6,9-12 and 1,3,5,7,8,13,14 partially.

because:

- ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):
  - ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):
  - ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.
  - ☒ no international search report has been established for the said claims Nos. 2,4,6,9-12 and 1,3,5,7,8,13,14 partially.
2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:
- ☐ the written form has not been furnished or does not comply with the standard.
  - ☐ the computer readable form has not been furnished or does not comply with the standard.

## IV. Lack of unity of invention

1. In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
- ☐ paid additional fees.
- ☐ paid additional fees under protest.

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- ☒ neither restricted nor paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
- ☐ complied with.
- ☐ not complied with for the following reasons:
4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☐ all parts.

☒ the parts relating to claims Nos. 1,3,5,7,8,13,14.

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims
	No:	Claims 1,3,5,7,8,13,14 NO
Inventive step (IS)	Yes:	Claims
	No:	Claims 1,3,5,7,8,13,14 NO
Industrial applicability (IA)	Yes:	Claims
	No:	Claims 1,3,5,7,8,13,14 YES

**2. Citations and explanations  
see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

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**Box III**

The present opinion refers to the following part of the application as originally filed:

Claims 1, 3, 5, 7, 8, 13 and 14 as far as the polymer formulations comprise ethylene vinylacetate co- or terpolymers or ethylene acrylic ester co- or terpolymers

**Box V**

1. The following document (D1) is referred to in this communication; the numbering will be adhered to in the rest of the procedure:

D1 WO-A-9920681 & EP-A-947541

3. The subject-matter of claims 1, 3, 5, 7, 8, 13 and 14 appears not to be novel in the sense of Article 33(2) PCT.

3.1 Subject matter of present claim 1 are compositions of

A) 10-80% crystalline propylene polymer

B) 10-85% EP(D)M rubber

D) 0.5-60% of an unsaturated compound selected from ethylene copolymers with vinylacetate or acrylic esters

D1 describes compositions of polymers A), B) and D), D) being a copolymer of ethylene with a polar group containing vinyl monomer in comparable ranges. The examples in D1 (table 1) disclose that the ethylene polymer is EVA or EMA. The compositions are crosslinked with peroxides. A flexibilizer for rubbers can be added. The compositions are used for car door trims.

All the technical features of claim 1 are therefore known from D1. Claim 1 is not novel

3.2 Claim 5 claims a similar composition to claim 1, but compound A) is selected from polyethylene or polypropylene. Such a composition is hence also disclosed in D1.

Claims 3, 7, 8, 13 and 14 all disclose technical features not mentioned in the abstract of D1. However, these features are disclosed in the english translation published as EP-A-

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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947541.

Claim 3 discloses the extension of EPDM with 30-60% oil. EP 947541 discloses the addition of 50-400 parts of oil as softener to 100 parts rubber (page 4, line 33-35)

Distinguishing technical feature of claim 7 is the addition of 0.1-1.5% peroxide. EP 947541 discloses in examples 1-4 the addition of 0.5% parts peroxide.

All the technical features of process claim 8 are either disclosed in the abstract of D1 or are evident from the translation.

Claims 13 and 14 claim car trims with skin layers of the composition of present application. The compositions of D1 are used as skin materials of automobile interior parts, for example door trims (EP 947541, page 8, line 30)

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Consequently, claims 3, 5, 7, 8, 13 and 14 cannot be regarded as novel.

**Box VIII**

4. Claim 1,5 and 8 do not appear clear in the sense of Art. 6 PCT.

4.2 Claim 5 dependant on claim 1 discloses compositions of 10-80% of a polyolefin being selected from also polyethylene. In claim 1, the polyolefin is polypropylene. Since claim 5 is dependant on claim 1, the selection of polyethylene as polyolefin makes the claim ambiguous. The applicant is asked to remove this ambiguity.

4.3 It is assumed that the applicant uses the term "unsaturated compound" to specify the polymers ethylene vinylacetate or ethylene acrylic ester. However, somebody skilled in the art would not associate these polymers with "unsaturated compound"s. This leads to ambiguity of the claims 1,5 and 8



pd  
"A FUNCTIONALIZED THERMOPLASTIC POLYMER COMPOSITION AND A  
PROCESS FOR ITS PREPARATION"

**Technical Field**

The present invention relates to a polyolefin-based functionalized  
5 thermoplastic polymer formulation which can be injection-molded,  
has a good hand (soft-touch), a high scratch-resistance, and is  
suitable to various forms of finishing, such as welding, gluing and  
painting. Particularly, the polymer formulation according to the  
invention is suitable to such uses as the external material - or skin - of  
10 trim panels for autovehicles.

The invention relates further to a process for the preparation of the  
aforementioned formulation.

**Background Art**

Various types of injection-moldable polyolefin-based polymers with a  
15 soft-touch are known in the art.

Application WO96/22327 describes a polymer formulation suitable for  
injection molding comprising 5-65% by weight of EP(D)M, 1-30% of  
polyalkanylene and their mixtures, grafted onto a matrix of  
polypropylene. This formulation has good processability and reduced  
20 stickyness, but, like other similar formulations, has little scratch-  
resistance and can not be subjected to welding, gluing or painting  
processes.

Another problem of known formulations is their processability.

Like the above mentioned ones, these materials are used to produce  
25 the external layer of skin in such products as car trim panels; the area  
of the panel is relatively wide while the thickness of the skin layer is  
very reduced. The material used should therefore have excellent

processability to be able to distribute itself in the die avoiding the form of "tiger-stripes" (advancement fronts) i.e. the stripes or signs due to the different rheological behavior of the polyolefin matrix with respect to the rubbery part.

- 5 The known formulations do not satisfy the above mentioned requirements and produce products having a high number of tiger stripes.

There is a need, therefore, to have formulations with the aforementioned improved features.

10 **Disclosure of the invention**

- Such purpose is achieved by the present invention which relates to a polyolefin-based thermoplastic polymer formulation characterized by comprising, by percentage of the total polymer weight, 10-80% of polypropylene and, grafted thereon, 10-85% of EP(D)M rubber, 0-40%  
15 of polybutadiene, and 0.5-60% of at least one unsaturated compound selected from: ethylene-vinyl acetate copolymers and terpolymers, NBR, acrylic ethylene-ester copolymers and terpolymers and polybutadiene polyurethanes or their precursors, the total amount of polybutadiene and unsaturated compounds not exceeding 60% by  
20 weight.

According to a preferential embodiment of the invention, the formulation contains polybutadiene-based polyurethanes obtained from precursors consisting of functionalized polybutadienes, i.e. polybutadienes having -OH, -NCO, -COOH groups.

- 25 According to a further embodiment the invention, the formulation contains the above mentioned precursory functionalized polybutadienes instead of or in addition to the polyurethane

obtained therefrom.

According to another preferential aspect, the formulation also comprises 5-30% of cellulose by weight of the total of the formulation.

The invention further relates to a composition for the preparation of a polymer formulation of the type above described, characterized according to Claim 5.

The invention further relates to a process for the production of a thermoplastic polymer formulation, characterized according to Claim 8.

The invention further relates to a trim element for vehicles, provided with a surface at least partly made with a material whose formulation is of the type described above. In a preferential embodiment, the product has an internal support layer and an external skin layer produced with the formulation of the invention.

The formulation according to the present invention has numerous advantages. The layer of "skin" obtained with the formulation of the invention is provided with particularly high scratch-resistance values, while also having excellent soft-touch and good mechanical characteristics.

The formulation presents excellent processability that makes it perfectly suitable both for being extruded in a flat layer, and for injection molding, and particularly for co-injection molding of products in which the formulation according to the invention constitutes the external layer or "skin."

A further advantage is that the products obtained from a material having the formulation of the invention can be subjected to finishing processes and particularly to painting, glueing and welding, e.g. high

frequency welding.

The thermoplastic polymer formulation according to the invention comprises, by percentage of the total weight of polymers ( i.e. excluding the weight of possible fillers), 10-80% of polypropylene, 0-40% of polybutadiene, 10-85% by weight of EP(D)M and 0,5-60% of an unsaturated compound selected from among ethylene-vinyl acetate copolymers and terpolymers (e.g. EVA), NBR (nitrile-butadiene rubber), acrylic ethylene-ester copolymers and terpolymers (e.g. EMA, EBA), and polybutadiene-polyurethanes or their precursors.

The total amount of unsaturated compounds (that is EVA etc., NBR, EMA, EBA etc. and polybutadiene-polyurethane) and of polybutadiene is less than or equal to 60% by weight of the polymers. The EP(D)M rubber and the polybutadiene and polybutadiene containing compounds are partially cross-linked and grafted onto the polypropylene; namely, the unsaturated compounds act as grafting units.

Precursors of the polybutadiene-polyurethanes are here meaning functionalised polybutadienes with terminal groups selected from -NCO, -OH and -COOH.

Polypropylenes suitable for use in the invention are propylene polymers and copolymers with isotactic index greater than 30%, such as the copolymers of propylene with one or more alpha-olefines having 2-10 atoms of carbon, as well as formulations of polypropylene obtained with sequential polymerization of polypropylene and of its mixtures with ethylene and/or alpha-olefines. Isotactic (co)polymers are preferred. The suitable propylene (co)polymers have a MFI (Melt Flow Index) that can vary over a wide range and is preferably within

the range of 0.1 and 60 at 230°C/ 21.6 N (ASTM 1238). Examples of suitable polypropylenes are those distributed commercially by Borealis under the proprietary name DAPLEN<sup>®</sup> and the codes DS10, US105A, CHC3007, FSC1012, and USC 1012.

5 The amount of polypropylene present is preferably between 15 and 50%.

EP(D)M rubbers (including EPR) suitable for use in the present invention are EP(D)M polymers and rubbers and their analogs; they are known in the art and are available commercially. Examples of suitable EP(D)M  
10 polymers are those commercially available from Enichem Elastomeri under the name of DUTRAL<sup>®</sup>; similar known examples of EP(D)M polymers are random copolymers having amorphous content greater than 50% by weight, for instance C<sub>2</sub>-C<sub>8</sub> type copolymers such as ENGAGE<sup>®</sup>, from Du Pont Dow Elastomers. The EP(D)M rubbers are, by  
15 preference, oil extended. Suitable oils for the extension are known in the art and commercially available, such as naftene and paraffin oils for instance. The amount of oil is generally between 40 and 60% by weight of the rubber and preferably around 50% by weight.

Preferably the amount of EP(D)M rubber present is 40-60% if an oil-  
20 extended rubber is used or 20-50% if dry.

Polybutadiene suitable to be used in the invention, is e.g. liquid polybutadiene containing at least 20% of structure 1,2, such as the one known as Lithene PH<sup>®</sup> of Revertex Ltd. Solid polybutadienes can also be used; this type of polybutadiene has a lesser content of 1,2  
25 structure (usually 0.5 to 12%) and is commercially available, e.g. from Enichem Elastomeri with the trade names Intene and Europrene. Solid polybutadiene being a rubbery material, its use will result in a lesser

amount of EP(D)M/EPR rubbers in the final formulation; e.g. if Intene or a similar compound is used the amount of EP(D)M rubber will decrease from 40-60% to 20-50%.

Preferably, the amount of polybutadiene is between 0.5% and 10%;  
5 when polyurethanes (TPU) obtained from polybutadienes as below disclosed are used in the formulation, unfunctionalized polybutadiene (i.e. the previously disclosed polybutadienes such as Lithene or Europrene) is preferably not present or is present in a reduced amount (up to 1.0%).

10 Suitable ethylene-vinyl acetate copolymers and terpolymers are those which contain between 6% and 26% of vinyl acetate by weight and preferably between 9% and 18% by weight. An example of ethylene-vinyl acetate copolymers is EVA, for instance that known as Escorene FL909, from Exxon. Suitable terpolymers are ethylene-vinyl acetate-  
15 maleic-anhydride, for instance that commercialized under the name of OREVAC by ELF ATOCHEM. Preferably the amount of EVA and terpolymers is between 10% and 25% and none of these polymers is present when polybutadiene-polyurethanes are provided in the formulation.

20 Suitable NBR polymers are butadiene-acrylonitrile copolymers with acrylonitrile content within the range 25-35%. An example of suitable NBR polymer is the one known as CHEMIGUM P86F from Goodyear, containing between 30.5 and 33.5% of acrylonitrile.

Suitable acrylic ethylene-ester copolymers are random ethylene-  
25 acrylic-ester copolymers such as EMA (ethylene-methyl acrylate) and EBA (ethylene-butyl acrylate) containing between 6 and 22% by weight of acrylate. Copolymers of this type are commercialized under

the LOTRYL name by ELF ATOCHEM. Other suitable acrylate polymers are ethylene-ester acrylic-maleic-anhydride terpolymers (with acrylate content between 6-22% by weight) commercialized under the name of LOTADER by ELF ATOCHEM.

5 Suitable polyurethane polymers are those unsaturated, based on polybutadiene, i.e. polymers obtained by reacting polybutadiene functionalized with isocyanide, hydroxyl or acidic terminal groups; examples of these prepolymers are reported below.

According to the invention, besides the polybutadiene-based-  
10 polyurethanes, their precursors may also be used, i.e. polybutadienes prepared with functional terminal groups selected from -OH, -NCO, -COOH. Such precursors can also be used alone, instead of the other mentioned unsaturated compounds. Preferably,

It is believed that these functionalized polybutadienes, like the other  
15 unsaturated compounds (polybutadiene-polyurethanes, EVA, NBR), behave in a way analogous to polybutadiene, i.e. that they partly cross-link and become grafted onto the polypropylene and the EP(D)M rubbers during the process of production of the formulation by means of vis breaking. In this way, polymers that are incompatible  
20 (polypropylene and polyurethane) are made compatible and a polymer formulation - i.e. a material - is obtained provided with polar groups, that make the material suitable to be painted, welded or glued. Preferably, the amount of polybutadiene-based polyurethane or its precursors is between 8% and 45%, the amount of rubber is 30-  
25 55% and the amount of polypropylene is 30-65%.

The total amount of unsaturated compounds, i.e. polybutadiene, EVA, EVA terpolymers, NBR, ethylene-acrylic-ester copolymers and

terpolymers, polyurethanes and precursors (polybutadienes with functional groups), is equal to a maximum of 60% by weight.

In an embodiment of the invention the composition that must be subjected to reactive extrusion (vis-breaking) comprises both  
5 polybutadiene functionalized with hydroxyl groups and polybutadiene functionalized with isocyanide groups. It is believed that the polybutadiene prepolymers react together during the visbreaking reaction to give a polyurethane grafted onto the polypropylene.

10 In another embodiment, the polybutadiene-based polyurethane to be used is first produced starting from mixtures of the following compounds: di-isocyanates, including polybutadiene functionalized with -NCO terminal groups, diphenylmethane di-isocyanate (MDI), toluene di-isocyanate (TDI) and diols such as butanediol, hexanediol,  
15 polybutadiene functionalized with hydroxyl terminal groups.

Polyurethane precursors of the type described above, suitable for the present invention are for instance those commercially available under the name KRASOL<sup>®</sup>, LBD and LBH, from KAUCUK (Czech Republic).

An example of the synthesis of a polybutadiene-based polyurethane  
20 starting from a polybutadiene isocyanate and two types of diol, a hexanediol and a hydroxylated polybutadiene, is reported in the following examples. It was found that polyurethanes obtained from polybutadiene isocyanate (a polybutadiene polyol carrying two TDI end groups) and polybutadiene polyol and/or a known diol (e.g. a  
25 short-chain diol) are perfectly mixable with the rubber and the polypropylene and have good mechanical properties.

A preferential embodiment of the invention provides for the presence



of 5-30% (by weight of the total formulation) of cellulose. Cellulose suitable for to the purpose is the pure or substantially pure one such as, for instance, that commercially available under the name ARBOCELL ZZ600 and BEM 600 from JRS (Germany).

5 Preferably, from 10% to 20 % of cellulose is used. It has been surprisingly found that the presence of cellulose results in a remarkable increase in the scratch-resistance of the product and in an improvement of the mechanical properties, without this negatively influencing the soft-touch features of the product.

10 The invention further protects the compositions for preparing a formulation of the type described above. The term formulation means the material, for instance in granules, powder or pellets, into which rubbers and unsaturated compounds have already been converted by reactive extrusion (vis-breaking) and presumably are partially cross-  
15 linked and grafted onto the polypropylene. The material of the formulation is ready to be molded and is already endowed with the desired characteristics.

The term composition means the mixture of polymers and additives before their processing by means of reactive extrusion (vis-breaking) to  
20 give the formulation of the invention.

According to the present invention the composition comprises, in an analogous way to that described above, as a percentage by weight of the total weight of the polymers, 10-80% of polypropylene, 10-85% of an EP(D)M rubber, 0-40% of polybutadiene, and 0,5-60% of at least  
25 one unsaturated compound selected from ethylene-vinyl acetate copolymers and terpolymers, NBR, ethylene-acrylic-ester copolymers and terpolymers, and polybutadiene-based polyurethanes or their

precursors, where the total amount of unsaturated compounds and polybutadiene is less than or equal to 60% by weight.

Beyond these components, the composition further comprises 0.1-1.5% of a radical-generating agent at the processing temperature of the composition, that is when the composition is subjected to vis-breaking.

The suitable polymers are those listed above.

Preferential agents able to generate radicals at the processing temperature of the composition are peroxides, such as, for instance, dicumyl peroxide, and 2,5-bis(tert-butylperoxy)2,5-dimethyl hexane.

Other suitable agents are non-peroxide initiators such as 2,3-dimethyl-2,3-diphenyl hexane and 2,3-dimethyl-2,3-diphenyl butane. All the radicals-generating agents are able to generate radicals, and therefore to start cross-linking, at the processing temperature of the composition, i.e. at the temperature reached by the composition when it has been melted, kneaded and is then extruded.

The process for the production of a thermoplastic polymer formulation according to the invention provides for the kneading in the molten state of a composition of the type described above, i.e. containing the radical-generating agents, at such a temperature as to activate said radical generating agents to create a plurality of active sites on the polypropylene chain. At least partial cross-linking of the rubbers and a greater or lesser degradation of the polypropylene is obtained this way. In this phase, known also as "visbreaking" or "reactive extrusion", the polybutadiene acts as a grafting agent and grafts onto the polypropylene and the rubbers. It is presumed that, similarly, unsaturated compounds EVA and ethylene-vinyl acetate-maleic anhydride terpolymers, NBR, ethylene-acrylic ester co- and

terpolymers and polybutadiene-based polyurethanes and their precursors also behave as grafting units on the polypropylene and the rubbers. The resultant composition will give a material with excellent mechanical and soft-touch characteristics and high scratch-resistance.

The temperature at which this process of reactive extrusion takes place is generally between 200 and 220 °C.

In order to avoid thermo-degradation phenomena of the components of the mixture, particularly during the reactive extrusion described above, antioxidants and stabilizers will be present in the usual amount, for instance between 0.1 and 1.5% by weight on the total weight of the polymers. These additives are known in the art; examples of suitable additives are sterically hindered phenols, secondary amines, thioethers, phosphites and phosphonites.

Preferably the amount of filler in the formulation is between 5-30%. Besides the cellulose described above, other vegetable fillers can be used, as well as additives and fillers such as for instance carbonate, silica and silicates like wollastonite, talc, caolin and dyes.

#### **Best modes for carrying out the invention**

The invention will be further illustrated with reference to the following examples.

#### **Example A- Synthesis of the polybutadiene based polyurethane**

175.2 parts of KRASOL LBD, a polybutadiene with isocyanate end groups from KAUCUK (Czech Rep. ), 22.55 parts of KRASOL LBH 3000, a polybutadiene with hydroxyl end groups and 2.25 parts of 2-ethyl-1,3-hexanediol are mixed and reacted at 80°C for 48 hours. A solid is obtained which is milled to be used in example 4.

**Example 1**

44.8 parts of DUTRAL CO 555 (an EPM (EPR) polymer oil-extended 45%), 35.8 parts of DAPLEN FSC 1012 Polypropylene (MFI 5 at 230°C/ 5Kg), 17 parts of EVA ESCORENE FL 909 (9.4% vinyl acetate content) from EXXON, 0.4 parts of a peroxide radical-generating agent di(t-butyl)peroxide-di-isopropylbenzene 40% on inactive support, 0.9 parts of antioxidant additives and 1.1 parts of LITHENE PH polybutadiene from REVERTEX CHEMICALS were mixed at 180-220°C in a Maris Ø 133 L/D= 40 co-rotating twin-screw extruder and then pelletized.

**Example 2**

48 parts of DUTRAL CS 9615 (an EPDM polymer oil-extended 45 %), 37.4 parts of DAPLEN FSC 1012 Polypropylene (MFI 5 at 230°C/ 5Kg), 10 parts of CHEMIGUM P86F from GOODYEAR (a butadiene-acrylonitrile rubber), 0.4 parts of peroxide radical-generating agent di(t-butyl) peroxide-di-isopropylbenzene 40 % on inactive support, 0.9 parts of antioxidant additives and 1.3 parts of LITHENE PH polybutadiene from REVERTEX CHEMICALS were mixed at 180-220°C in a Maris Ø 133 L/D= 40 co-rotating twin-screw extruder and then pelletized.

**Example 3**

52 parts of DUTRAL CS 9615 (an EPDM polymer oil-extended 45 %), 42 parts of Polypropylene DAPLEN FSC 1012 (MFI 5 at 230°C/ 5Kg), 0.4 parts of peroxide radical-generating agent di(t-butyl) peroxide-di-isopropylbenzene at 40 % on inactive support, 0.4 parts of antioxidant additives, 1 part of LITHENE PH polybutadiene from REVERTEX CHEMICALS, 4 parts of KRASOL LBD (a polybutadiene with isocyanate end groups) and 0.2 parts of 2-ethyl-1,3-hexanediol (Aldrich)

were mixed at 180-220°C in a Maris Ø 133 L/D= 40 co-rotating twin-screw extruder and then pelletized.

**Example 4**

48 parts of DUTRAL CS 9615 (an EPDM polymer 45% oil-extended),

5 40 parts of Polypropylene DAPLEN FSC 1012 (MFI 5 at 230°C/ 5Kg), 10  
parts of polybutadiene-based Polyurethane synthesized as described  
above, 0.4 parts of peroxide radical-generating agent di(t-butyl)  
peroxide-di-isopropylbenzene at 40% on inactive support, 0.7 parts of  
antioxidant additives and 0.9 parts of polybutadiene LITHENE PH of the  
10 REVERTEX CHEMICALS

were mixed at 180-220°C in a Maris Ø 133 L/D= 40 co-rotating twin-screw extruder and then pelletized.

The following table reports the values of some mechanical characteristics of the formulations obtained.

15 Table 1

	Example 1	Example 2	Example 3	Example 4
MFI				
at 230°/21 6N	8.8	5.5	14.6	9.5
Shore D	32	25	25	23

The materials obtained were molded by means of co-injection molding technique on 1850-ton Mir press at a temperature of about 220°C, to give products in which the formulation constitutes the  
20 external layer of skin.

The materials have good processability and distribution of the materials, as well as reduced fogging and improved scratch-resistance.

Further, it was observed a substantial reduction of the advancement

fronts (tiger-stripes) usually due to the different rheological behavior of the polyolefin matrix with respect to the rubber portion.

The polymer formulation as obtained is particularly suitable for the production of the skin of trim elements for cars where by the term

5 "components " are understood all the known components for cars, such as panels, bridges, console, and coverings generally.

**CLAIMS**

1. A polyolefin-based thermoplastic polymer formulation characterized by comprising, by weight of the total weight of the polymers, 10-80% of polypropylene, 10-85% by weight of EP(D)M rubber, 0-40% of polybutadiene, and 0,5-60% of at least one unsaturated compound selected from: ethylene-vinyl acetate copolymers and terpolymers, NBR, ethylene-acrylic ester copolymers and terpolymers, and polybutadiene-based polyurethanes or their precursors, or mixtures thereof, the maximum total amount of polybutadiene and unsaturated compounds being 60% by weight, said polybutadiene and unsaturated compounds being grafted onto the polypropylene and the EP(D)M rubber.
2. A formulation according to Claim 1, in which said precursors of polybutadiene-based polyurethanes are one or more polybutadienes provided with terminal groups selected from -NCO, -OH, -COOH.
3. A formulation according to Claim 1 or 2, in which said EP(D)M rubbers are oil extended at 30-60% by weight.
4. A formulation according to any previous Claim, characterized by the polybutadiene-based polyurethane being the reaction product of a polybutadiene derivative having an -NCO group with a polybutadiene derivative having a terminal group selected from -OH and -COOH and/or with a diol known in the art.
5. A composition for the preparation of a formulation according to any preceding Claim, characterized by comprising by weight out of the total weight of the polymers, 10-80% of a polyolefin selected from polyethylene and polypropylene, 10-85% by weight of an EP(D)M rubber, 0-40% of a polybutadiene, 0,5-60% of at least one unsaturated

compound selected from ethylene-vinyl acetate copolymers and terpolymers, NBR, ethylene-acrylic ester copolymers and terpolymers, and polybutadiene-based polyurethanes or their precursors the maximum total amount of polybutadiene and of unsaturated compounds being 60% by weight.

6. A composition according to Claim 5, comprising 0,5-20% of one or more polybutadienes provided with terminal groups selected from ;

-NCO, -OH, -COOH.

7. A composition according to claim 5 or 6, further comprising 0.1-1.5% of a radical-generating agent at the processing temperature of the composition.

8. A process for the production of a thermoplastic polymer formulation, characterized by mixing a composition comprising, by weight of the total weight of the polymers, 10-80% of a polyolefin selected from polyethylene and polypropylene, 10-85% by weight of an EP(D)M rubber, 0-40% of a polybutadiene, 0,5-60% of at least one unsaturated compound selected from ethylene-vinyl acetate copolymers and terpolymers, NBR, ethylene-acrylic ester copolymers and terpolymers, and polybutadiene-based polyurethanes or their precursors, the maximum total amount of polybutadiene and of unsaturated compounds being 60% by weight, and 0,1-0,6% of at least one agent generating radicals, at a temperature such as to activate said radical-generating agent to effect a partial cross-linking of at least some of the polymers present.

9. A process according to Claim 8, in which at least one polybutadiene provided with terminal groups selected from -OH,



-NCO and -COOH, is used as unsaturated compound.

10. A process according to Claim 8 or 9, in which said polybutadiene-based polyurethane is prepared by reaction of -NCO functionalized polybutadienes with a -OH or -COOH polybutadienes and/or a diol.

11. A process for the preparation of an unsaturated polybutadiene-based polyurethane, in which a polybutadiene prepolymer provided with isocyanate end groups is reacted with one or more diols.

12. A process for the preparation of an unsaturated polybutadiene-based polyurethane, in which a polybutadiene prepolymer provided with hydroxyl terminal groups is reacted with one or more diisocyanates.

13. A trim element for autovehicles, characterized by having an external surface made at least partly with a thermoplastic material having a formulation according to any Claim 1 to 4.

14. A trim element for autovehicles according to Claim 13, comprising an internal support layer and an external skin layer, said external skin layer corresponding to said surface.

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Francesco [IT/IT]; Via Cavour, 1, I-22070 Guappate (IT). ARRIGHI, Franca [IT/IT]; Via ai Prati, 4, I-22070 Bulgarograsso (IT).

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(74) Agent: **GISLON, Gabriele; Marietti e Gislon S.r.l.**, Via Larga, 16, I-20122 Milan (IT).

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(71) Applicant (*for all designated States except US*): **JOHNSON CONTROLS AUTOMOTIVE S.R.L. [IT/IT];**  
Strada Statale 11, Padana Superiore 2/B, I-20063 Cernusco (IT).

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(72) Inventors; and  
(75) Inventors/Applicants (*for US only*): **MASCIA;**

(54) Title: **A FUNCTIONALIZED THERMOPLASTIC POLYMER COMPOSITION AND A PROCESS FOR ITS PREPARATION**

(57) Abstract: A polyolefin-based thermoplastic formulation giving products with soft-touch and functionalized to be welded and painted comprises, by weight of the total weight of the polymers, 10-80 % of polypropylene, 10-85 % by weight of EP(D)M rubber, 0-40 % of polybutadiene, and 0.5-60 % of at least one unsaturated compound selected from: ethylene-vinyl acetate copolymers and terpolymers, NBR, ethylene-acrylic ester copolymers and terpolymers, and polybutadiene-based polyurethanes or their precursors, or mixtures thereof; with the proviso that the total amount of polybutadiene and unsaturated compounds is equal or less than 60 % by weight. The formulation is prepared via visbreaking of the above listed compounds with radical-generating agents.

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- (21) International Application Number: PCT/EP00/05128
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- (71) Applicant (*for all designated States except US*): JOHN-SON CONTROLS AUTOMOTIVE S.R.L. [IT/IT]; Strada Statale 11, Padana Superiore 2/B, I-20063 Cernusco (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): MASCIA, Francesco [IT/IT]; Via Cavour, 1, I-22070 Guanzate (IT). ARRIGHI, Franca [IT/IT]; Via ai Prati, 4, I-22070 Bulgarograsso (IT).
- (88) Date of publication of the international search report:  
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(54) Title: A FUNCTIONALIZED THERMOPLASTIC POLYMER COMPOSITION AND A PROCESS FOR ITS PREPARATION

(57) Abstract: A polyolefin-based thermoplastic formulation giving products with soft-touch and functionalized to be welded and painted comprises, by weight of the total weight of the polymers, 10-80 % of polypropylene, 10-85 % by weight of EP(D)M rubber, 0-40 % of polybutadiene, and 0.5-60 % of at least one unsaturated compound selected from: ethylene-vinyl acetate copolymers and terpolymers, NBR, ethylene-acrylic ester copolymers and terpolymers, and polybutadiene-based polyurethanes or their precursors, or mixtures thereof; with the proviso that the total amount of polybutadiene and unsaturated compounds is equal or less than 60 % by weight. The formulation is prepared via visbreaking of the above listed compounds with radical-generating agents.

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# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>7526/675 (GG)</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 00/05128</b>	International filing date (day/month/year) <b>05/06/2000</b>	(Earliest) Priority Date (day/month/year) <b>04/06/1999</b>

Applicant

**JOHNSON CONTROLS AUTOMOTIVE S.R.L.**

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☒ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.     --    

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 00/05128

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1,3,5,7,8,13,14 (all partially)

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1, 3, 5, 7, 8, 13, 14 (partially)  
polymer formulations comprising ethylene vinylacetate co- or terpolymers or ethylene acrylic ester co or terpolymers
2. Claims: 1, 3, 5, 7, 8, 13, 14 (partially)  
polymer formulations comprising NBR
3. Claims: 1, 3, 5, 7, 8, 13, 14 partially, 2 , 4 , 6, 9-10  
polymer formulations comprising polybutadiene based polyurethanes or their precursors
4. Claims: 11, 12  
as far as processes for the preparation of polybutadiene based polyurethanes are concerned

## INTERNATIONAL SEARCH REPORT

International Application No

PCT 00/05128

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 20681 A (MITSUBISHI) 29 April 1999 (1999-04-29) abstract; examples 1-4; table 1	1,3,5,7, 8,13,14
P,X	& EP 0 941 541 A 6 October 1999 (1999-10-06) page 8, line 30; examples 1-4; table 1	1,3,5,7, 8,13,14
A	WO 96 22327 A (COMMER SPA ;SIANO DANTE (IT); MASCIA FRANCESCO (IT)) 25 July 1996 (1996-07-25) cited in the application page 9, last paragraph -page 10, paragraph 1; example 6	13,14
A	US 4 948 840 A (BERTA DOMINIC A) 14 August 1990 (1990-08-14) examples 1-3,7-14	1,5

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

21 August 2000

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

SCHMIDT, H

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT 00/05128

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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